



## Pyrolysis of Sorghum straw: Effect of temperature and reaction environment on the product behavior

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### ABSTRACT

Sorghum straw is a massively produced agricultural waste in India. Thermochemical conversion can be used to convert this waste into the useful chemicals. This paper illustrates the production of valuable hydrocarbon via slow pyrolysis of sorghum straw biomass in a bench-scale reactor in  $N_2$  and  $CO_2$  environments. The pyrolysis experiments were conducted at the temperatures of 300, 350, 400, and 450°C, and atmospheric pressures. The objective of the work was to analyze the effect of temperature and reaction environment on the product behavior. The organic phase of the bio-oil was found to be mainly composed of phenols, furans, and ketones. Maximum yield of bio-oil was obtained at 350°C for  $N_2$  environment, and at 400°C for  $CO_2$  environment. The bio-oil obtained in  $CO_2$  environment was found to be more abundant in phenols and furans, while being relatively leaner in ketone group compounds in comparison to that obtained in the  $N_2$  environment.

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### 1. Introduction

In the contemporary time, the world economy is dependent on petroleum and petroleum-derived products. The price volatility of petroleum feedstock and emergent concerns over the environmental impacts associated with the production of petroleum-derived fuels and chemicals have created interest in finding renewable substitutes that can be used without any major changes to the current fuel distribution and utilization infrastructure. Production of liquid fuels and chemicals from lignocellulosic biomass is a potential solution to the problem. 'Lignocellulosic biomass' refers to a wide range of feedstocks such as agricultural residue, plant wood, waste from wood processing industries, and dedicated energy crops, which are primarily composed of hemicellulose, cellulose, and lignin biopolymers. These under-exploited feedstocks have an enormous potential and can be considered as the suitable option for meeting the demand and insurance of future energy/fuel/biochemical supply sustainably. The modernization of technologies leading to more proficient biomass production and conversion is one possible route for efficient utilization of biomass resources. Agricultural biomass is a relatively broad category of biomass that includes the food based portion (oil and simple carbohydrates) of crops (such as corn, sugarcane, beets) as well as the non-food based part (complex carbohydrates) of crops (such as the leaves, stalks, cobs, stover, trimmings, husk, straw, etc.), perennial grasses, and animal waste. These feedstocks can be efficiently utilized via conversion into more suitable forms such as bio-oil (Koçar and Civas, 2013).

Currently, 'Pyrolysis', a thermochemical conversion route is emerging as a promising technology for the production of bio-oil. Pyrolysis is the thermal decomposition of a feed substance into smaller fragments by heating in the absence of oxygen. The main benefit of pyrolysis process is that the liquid fuel produced can be easily stored and transported. Apart from the energetic use of bio-oil, a unique advantage of bio-oil over other renewable energies is that an array of value-added chemicals can be isolated from it. Several industrially important organic compounds which are conventionally synthesized from crude oil can be obtained in the pyrolytic oils, thus providing a green route for their production and efficient utilization of carbon. Another approach to make the process environment-friendly is to use carbon dioxide atmosphere, which is a leading greenhouse gas for conducting pyrolysis. Incorporation of carbon dioxide in pyrolysis products can lead to increase in carbon content of the pyrolysis products, along with a simultaneous reduction in the greenhouse gas emission.

Pyrolysis of agricultural waste is desirable, as the cultivation of crops has less demand of area and cultivation period, compared to wood biomass. Also, a large part of the crop body is non-edible and goes as waste. Straw is an agricultural by-product, the dry stalks of cereal plants after the grain and chaff have been removed. Straw can make up to about half of the yield of cereal crops (Dhyani et al., 2017; Dhyani and Bhaskar, 2017).

Sorghum is a genus of flowering plants from the grass family *Poaceae*, which is an important staple food in dry parts of Asia and Africa, because

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of less water consumption, drought tolerance, and easy production. Sorghum (*Sorghum bicolor*) is one of the major cereal crops consumed in India after rice (*Oryza sativa*) and wheat (*Triticum aestivum*), making India the second largest producer worldwide. Sorghum stover is widely used as fodder and it often gains importance over grain in some areas, particularly where growing conditions are unfavorable (Kleih et al., 2000). In the year 2016, India reported a production of 5.5 million Tons of sorghum (India Sorghum Production by Year, 2016). With such high production comes an enormous quantity of waste available for being converted into biofuel and other valuable hydrocarbons. Cardoso et al. (2011) reported a high yield of phenols, and other oxygenated hydrocarbons such as organic acids, aldehydes, and ketones in the bio-oil obtained from sorghum bagasse subjected to fast pyrolysis from ambient temperature to 1023 K. Piskorz et al. (1998) conducted fast pyrolysis of sweet sorghum and sweet sorghum bagasse, and obtained high concentration of levoglucosan, formic acid/formaldehyde and pyrolytic lignin in the bio-oil obtained from the pyrolysis of sweet sorghum bagasse in comparison to that obtained from sweet sorghum. However, these studies can not define the product behavior of bio-oils obtained from pyrolysis of straw obtained from the Indian genus of sorghum.

In the present work, slow pyrolysis of sorghum straw was carried out in a bench scale reactor in nitrogen and carbon dioxide environments, to study the effect of temperature and reaction environment on the product behavior. The primary intention of the study was to identify the temperature of maximum bio-oil yield, to characterize the organic fraction of the bio-oil using gas-chromatography/ mass-spectroscopy (GC/MS), Fourier transform-infrared spectroscopy (FT-IR), and nuclear magnetic resonance spectroscopy (NMR), and to study the influence of reaction environment on the product chemistry. The biochar was also analyzed using FT-IR and elemental analysis (CHNS).

## 2. Materials and Methods

### 2.1. Feedstock

Sorghum straw was collected from CSIR-Indian Institute of Petroleum, Dehradun. The feedstock was ground and sieved to < 630-micron size, before conducting pyrolysis experiments. 10 g ground feed sample was used for pyrolysis studies, while in the Thermogravimetric analysis (TGA), approximate 5 mg sample was used.

### 2.2. Experimental setup

Pyrolysis experiments were conducted at 300, 350, 400, and 450°C, in a laboratory scale pyrolysis unit, the schematic diagram of which has been illustrated in figure 1. The temperature regime for the experiment was chosen based on the thermal decomposition pattern obtained from thermogravimetric analysis (TGA). Each pyrolysis experiment was initiated with a non-isothermal regime, in which feed was heated at 20 °C/min until the end temperature was reached, where the temperature was held constant for an hour. The reactor temperature was controlled using a PID temperature controller. Two sets of experiments were conducted with N<sub>2</sub> and CO<sub>2</sub> environments respectively. N<sub>2</sub>/CO<sub>2</sub> gases were purged into the reactor at a flow rate of 40 ml/min, to create an inert atmosphere and also to carry the products of pyrolysis from reactor to an external condenser, where bio-oil was condensed and separated from the non-condensable gasses. The condensed bio-oil was collected in a measuring cylinder. The condenser temperature was set at 5°C, and the uncondensed products were passed through a methanol filled impinger. The impinger solution was also characterized via GC/MS to check the condenser efficiency. The organic and aqueous phases of the bio-oil were separated using diethyl ether (DEE) solvent.

### 2.3. Characterization methods

Thermogravimetric analysis (TGA) was carried out in a DTG-60 unit (Shimadzu, Japan). TGA was performed to provide decomposition pattern, based on which the experiments were conducted. ASTM standards E871, E1755, and E872 were followed for the determination of moisture (M), ash, and volatile matter (VM) respectively. In addition to this, the fixed carbon (FC) content was calculated by difference using the balance:

$$\%FC = 100 - (\%M + \%VM + \%Ash) \quad (1)$$

The composition of the organic fraction of the bio-oil was analyzed using Agilent 7890B GC/MS. An HP-1 column (25 m x 0.32 mm x 0.17 μm) was used for the separation. Helium gas, at a flow rate of 1 ml/min was used as the carrier gas inside the column. An isothermal oven program was set at 50°C for 2 min, followed by a heating rate of 5°C/min till 300°C where it was held for 5 min. The injected volume was 1 μl with a

split ratio of 1/100. The 1H-NMR spectra were recorded by Bruker Avance 500 Plus instrument using a CDCl<sub>3</sub> solvent to characterize the protons present in the bio-oil. The functionality of bio-oil obtained at a temperature of maximum liquid yield (or optimum temperature) was compared to biochar obtained at the same temperature and parent feedstock, using FT-IR spectroscopy. The FT-IR spectra were recorded on Nicolet 8700 FTIR spectrometer with the sample diluted in KBr. The equipment resolution was 4 cm<sup>-1</sup> and 36 scans. The elemental composition (CHNS) of biomass and biochar were determined by Elementer Vario Microcube CHNS Analyzer. Higher heating value (HHV) of the feed and the biochar were calculated using the empirical correlation by Chaniwala and Parikh (2000):

$$HHV, \text{ MJ/kg} = 0.3491(C) + 1.1783(H) - 0.10(S) - 0.0134(O) - 0.0151(N) - 0.0211(A) \quad (2)$$

The yield of pyrolysis products and total conversion was calculated using equation (3) to (6):

$$\text{Bio-oil yield} = (C2 - C1) * 100/F \quad (3)$$

$$\text{Biochar yield} = (R2 - R1) * 100/F \quad (4)$$

$$\text{Yield of non-condensable gases} = 100 - \text{Bio-oil yield} - \text{Biochar yield} \quad (5)$$

$$\text{Conversion} = \text{Yield of Bio-oil} + \text{Yield of non-condensable gases} (6)$$

where, C1: Initial weight of the measuring cylinder, g

C2: Weight of measuring cylinder after completion of reaction, g

R1: Initial weight of reactor, g

R2: Weight of reactor + residual biochar after completion of reaction, g

F : Weight of feed (10 g)

## 3. Results and discussion

### 3.1. Feedstock analysis

The physicochemical properties of the sorghum straw sample are summarized in table 1. It can be observed that the feedstock has a high volatile content of 65.38% (70.85% on moisture free basis) while a low fixed carbon ratio. The low fixed carbon content indicates a lower lignin composition in the biomass. Although ash is undesirable in the feedstock, the ash composition of sorghum straw matches with the ash composition of other agricultural wastes (Dhyani and Bhaskar, 2017). Ultimate analysis results revealed a very high oxygen content, higher than the carbon content. High O/C ratio leads to a decrease in the heating value of the feedstock. The empirical formula of sorghum straw based on the elemental analysis is CH<sub>1.925</sub>O<sub>0.875</sub>N<sub>0.008</sub>S<sub>0.007</sub>.

**Table 1.** Physicochemical properties of sorghum straw

Proximate analysis (wt.%, wet basis)	
Moisture, wt%	7.72
Volatiles, wt%	65.38
Fixed carbon, wt%	19.77
Ash, wt%	7.13
Elemental analysis (wt.%, dry-ash-free basis)	
C, wt%	42.44
H, wt%	6.81
N, wt%	0.40
S, wt%	0.83
O, wt% (By difference)	49.51
Heating value	
HHV, MJ/kg	20.58

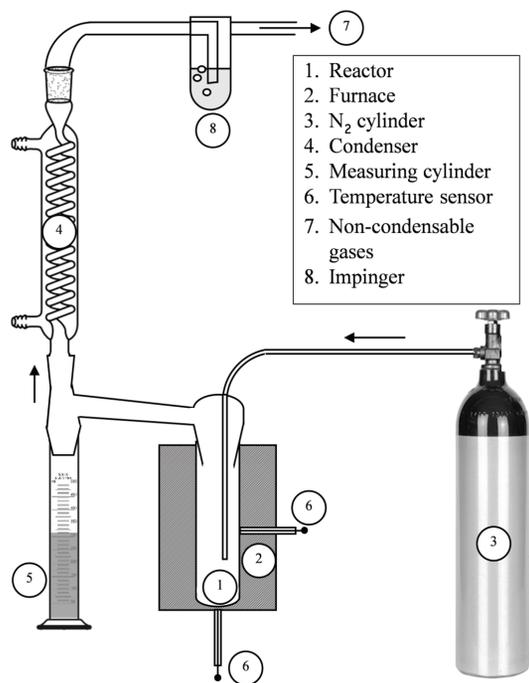


Figure 1. Schematic layout of the pyrolysis unit

From the TGA curve (figure 2) it can be perceived that the maximum decomposition of sorghum-straw takes place in a temperature range of 300 to 400°C. Major fractions of hemicellulose and cellulose, but only a small fraction of lignin decompose in this range (Carrier et al. 2011). This phenomenon was followed by slow weight loss until 600°C, which can be attributable to the continuous volatilization of biomass caused by the further breakdown of C-C and C-H bonds. Decomposition at temperatures higher than 600°C progressed slowly because of slow rate of lignin breakdown (Liang et al., 2014).

### 3.2. Yield of pyrolysis products

The yields of bio-oil, biochar, and non-condensable gasses, calculated on a weight basis for both N<sub>2</sub> and CO<sub>2</sub> environments are graphically illustrated in figure 3. It can be observed that while the maximum liquid yield in the N<sub>2</sub> environment was obtained at 350°C, while in case of CO<sub>2</sub> environment it shifted to 400°C. The maximum liquid yield in CO<sub>2</sub> environment (43.5%) was also higher than that obtained in the N<sub>2</sub> environment (38.25%). The yield of biochar obtained as the residue in the pyrolysis reactor was also higher in case of CO<sub>2</sub> environment. In case of the N<sub>2</sub> environment, the total conversion (yield of liquid + gasses) was observed to increase with increase in the reaction temperature, this can be attributed to the secondary cracking reactions of the previously formed condensable products (Krishna et al., 2016). Contrary to this, the total conversion in the case of reaction in CO<sub>2</sub> environment was observed to decrease until 400°C, implying that incorporation of CO<sub>2</sub> in pyrolysis products lead to production of condensable compounds. A detailed profile of the condensable products (bio-oil) was obtained by GC/MS analysis.

### 3.3. Bio-oil characterization

#### 3.3.1. GC/MS analysis

The compounds identified in GC/MS of the organic fraction of the bio-oil were classified as acids, alcohols, ketones, aromatics, phenols, furans, and their derivatives. The presence of furans, acids, hydrocarbons, carbonyl compounds, and alcohols is generally due to the holocellulose fraction and aromatic ethers while phenolic compounds originate from the lignin fraction present in the feedstock. Phenolic compounds constituted a major portion of the produced bio-oil (up to 53.85% in N<sub>2</sub> environment and 53.26% in CO<sub>2</sub> environment), which was followed by furans (up to 25.66% in N<sub>2</sub> environment and 34.16% in CO<sub>2</sub> environment), and ketones (up to 14.71% in N<sub>2</sub> environment and 12.59% in CO<sub>2</sub> environment) (figure 4). Detailed GC/MS data has been presented in table 2. More furans were obtained at lower temperatures, due to the degradation of holocellulose fraction of the biomass. The product behaviour was also observed to be affected by temperature. On increasing the temperature from 300°C to 450°C the yield of phenols and its derivatives was increased in both the environments. In the phenolic compounds, phenolic ethers

constituted the major part followed by alkyl phenols and monomeric phenol. Aromatics such as benzene, alcohols, and acids were also present in minor quantities, also supported by <sup>1</sup>H-NMR data. Use of CO<sub>2</sub> environment lead to an increase in the yield of phenolic ethers and furans, while the yield of ketones decreased in CO<sub>2</sub> environment. High yield of phenolics has also been reported in the literature for the pyrolysis of rice straw (Balagurumurthy et al., 2015) and barley straw (Serés-Aspax et al., 1985). The GC/MS analysis of impinger solution didn't show any compound other than methanol solvent, indicating that none of the condensable pyrolysis products escaped the system as non-condensable gases.

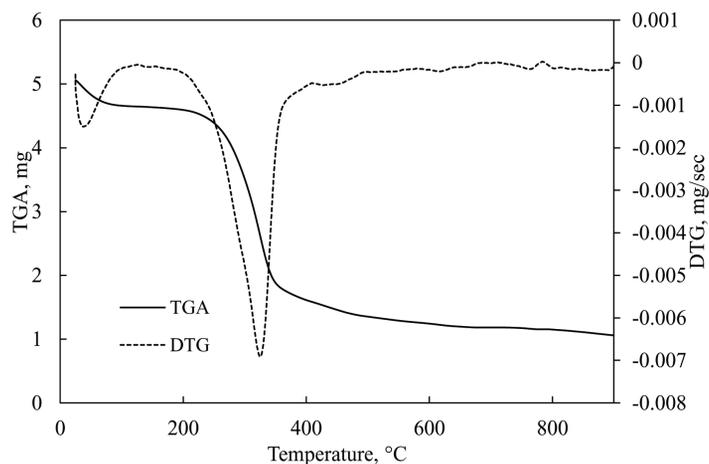


Figure 2. TGA/DTG analysis of sorghum straw

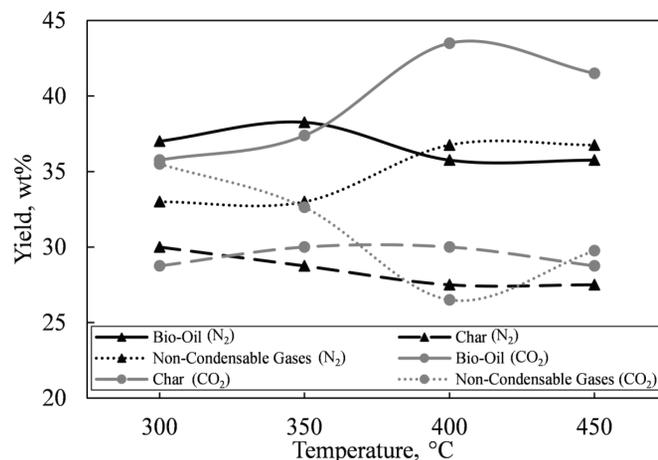


Figure 3. Yield of products obtained from pyrolysis

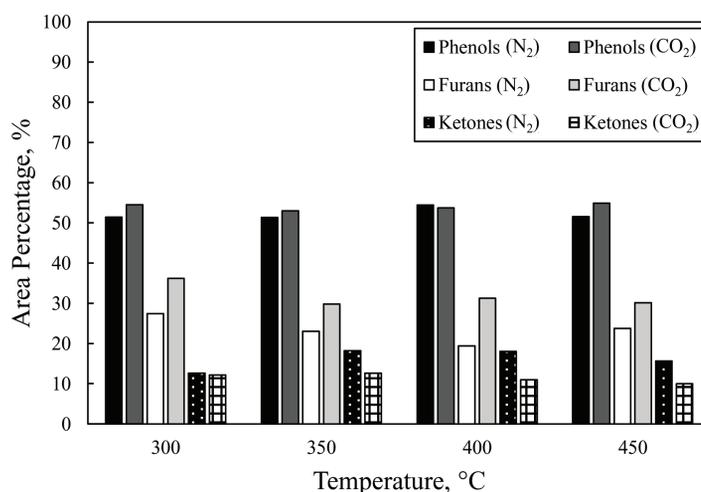


Figure 4. Comparison of area percentage of major bio-oil components obtained at different reaction conditions

The compounds obtained in the bio-oil are of widespread importance. The phenolic compounds present in the bio-oil such as methylphenols and methoxyphenols have a significant potential, in food, pharmaceutical and paint industries (Horne and Williams, 1996; Stoikos, 1991). Furfuryl alcohol is a useful chemical intermediate in the manufacture of furan resin prepolymers that are exploited in thermoset polymer matrix composites, cement, adhesives, casting resins and coatings. Furfuryl alcohol is also used for the production of tetrahydrofurfuryl alcohol which is used as a nonhazardous solvent in agricultural formulations and as an adjuvant to help herbicides penetrate the leaf structure. Furfural is an important chemical solvent which can be used to make other furan chemicals, such as furoic acid, via oxidation, and furan itself via palladium catalyzed vapor-phase decarbonylation (Ozer, 2015). Cyclopentenone is useful in the production of cyclopentenone prostaglandins, a class of biologically active compounds which possess potent anti-inflammatory, anti-neoplastic, and anti-viral activity (Straus and Glass, 2001).

### 3.3.2. <sup>1</sup>H-NMR analysis

Proton NMR spectroscopy gives information about the types of protons present in the compound hence, revealing the basic structure of all the complex organic species present in the bio-oil. For the comparison of bio-oils, the <sup>1</sup>H NMR spectrums of the bio-oil obtained at an optimized pyrolysis condition of 350°C in case of nitrogen environment and 400°C in case of carbon dioxide environment were considered (figure 5 (a)-(c)). The highly shielded region of 0.50-1.50 ppm corresponds to the methyl protons on the aliphatic carbon, where 24.31% of protons are present in case of nitrogen and 26.21% in case of carbon dioxide. The region of 1.50-3.00 ppm is known for the methylene and methine protons of the aliphatic carbon. Almost same number of protons resonate in both the environments, 37.66% in case of nitrogen and 37.64% in case of carbon dioxide. In region of 3.0-4.5 ppm, the protons present are attached to some heteroatoms, probably oxygen, 17.24% protons for nitrogen and 19.51% protons for carbon dioxide. These protons indicate the existence of hydroxyl or alkoxide groups, that could be due to aromatic ethers similar to those from lignin derived methoxy phenols or the molecules derived from carbohydrates. The next region of 4.50-6.00 ppm is for the olefinic protons that are due to unsaturation present in the cyclic compounds such as cyclopentene and its derivatives. According to the results of the GC-MS, high number of aromatics are present in case of nitrogen when compared with that of carbon dioxide. Around 4.59% of protons resonate in case of nitrogen whereas, just 2% of protons resonate in carbon dioxide environment. The region of 6.0-9.0 ppm is the aromatic region. Peak in this zone can be attributed to the protons present in benzene or its derivatives or those in heterocyclic aromatic compounds like furans. 14.88 % of protons resonate in case of nitrogen whereas, 14.96% of protons in carbon dioxide environment. The appearance of these peaks along with those of hydroxyl and alkoxide groups, indicates the presence of large number of substituted phenolic compounds like cresol, catechol, phenols, alkyl phenols, and phenolic ethers in both the atmospheres which agrees with the result obtained from GC-MS. The most downfield region from 9.0-10.0 ppm corresponds to the protons mainly on aldehydes and at times also from carboxylic acid. Protons observed in this region are almost imperceptible, indicating very low concentration or absence of these compound.

### 3.4. Analysis of char

The proximate and ultimate analysis biochar obtained at the optimum liquid yield temperature (350°C in N<sub>2</sub> and 400°C in CO<sub>2</sub> atmosphere) is presented in table 3. In comparison to the proximate analysis of the feedstock, a decrease in the volatile fraction and an increase in fixed carbons can be observed in both the biochar samples. Such transformation is obvious as pyrolysis leads to the devolatilization of the biomass. Since only traces of ash escape the pyrolysis environment, the produced biochar has high ash content. The ultimate analysis of the biochar reveals the alterations that occur in the chemical composition of biomass when it is pyrolyzed, the carbon content was observed to increase in both the reaction environments, while hydrogen and oxygen content showed a decline compared to the parent feedstock. It can be interpreted that during pyrolysis, the liberated compounds contained higher proportions of oxygen and hydrogen than carbon, thus reducing the H/C and O/C ratios of the residual biochar. Less carbon and hydrogen content, and consequently less HHV was observed in the biochar obtained in CO<sub>2</sub> atmosphere. This can be attributed to the fact that the char samples corresponding to the temperatures of maximum liquid yields were chosen for comparison, and the temperatures of maximum liquid yield are different in both the environments. Since, the maximum liquid yield was obtained at 400°C, in the case of CO<sub>2</sub> atmosphere in comparison to 350°C in the case of N<sub>2</sub>

atmosphere, some of the solid carbon transformed into condensable hydrocarbons.

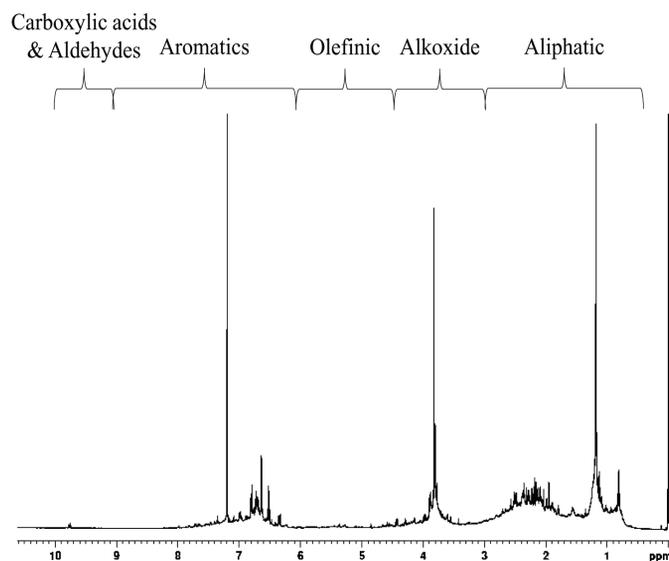


Figure 5(a)

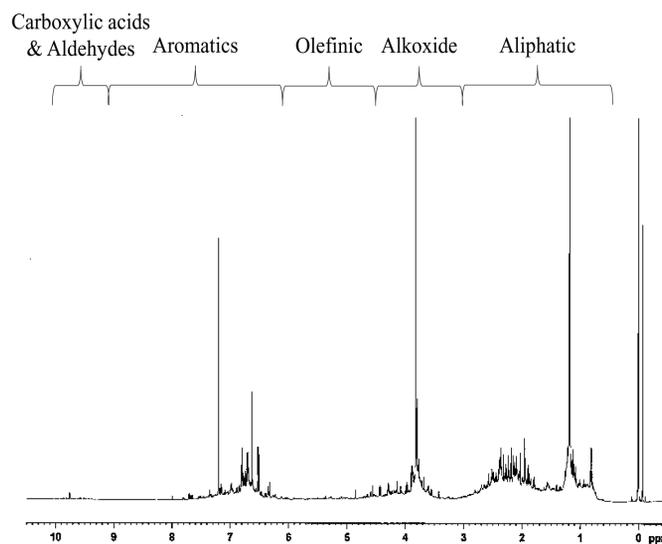
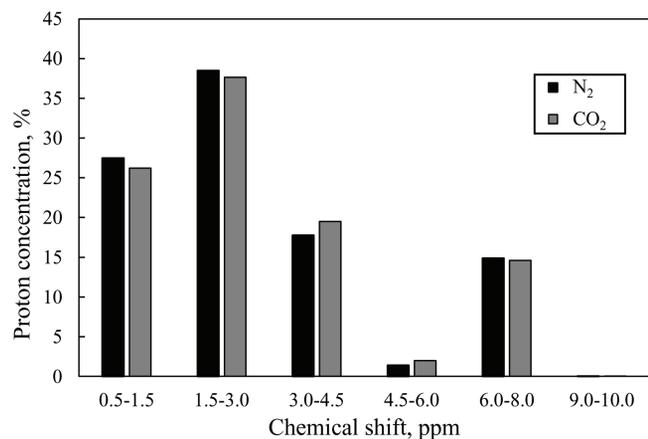


Figure 5 (b)

**Figure 5.** Results of <sup>1</sup>H-NMR analysis of bio-oil: (a) <sup>1</sup>H-NMR spectrum of bio-oil obtained in N<sub>2</sub> atmosphere, (b) <sup>1</sup>H-NMR spectrum of bio-oil obtained in CO<sub>2</sub> atmosphere



**Figure 5.** (c) comparison of proton concentration at different chemical shift

Table 2. Results of GC/MS analysis of the bio-oil

Compound	Area Percent (%)							
	300 °C		350 °C		400 °C		450 °C	
	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
<i>Acids</i>								
Benzoic acid, 4-hydroxy-3-methoxy-	---	---	1.43	---	---	---	---	---
Butanoic acid	---	---	---	---	0.73	---	---	---
Propanoic acid	---	---	---	---	---	---	1.76	---
<b>Total</b>	---	---	<b>1.43</b>	---	<b>0.73</b>	---	<b>1.76</b>	---
<i>Aromatics</i>								
1,2,3-Trimethoxybenzene	1.06	---	---	---	---	---	---	---
4-Ethylbiphenyl	---	---	---	---	1.38	---	---	---
Bis(2-ethylhexyl) phthalate	---	---	1.66	---	---	---	---	---
Phthalic acid, di(2-propylpentyl) ester	1.23	---	---	---	---	---	---	---
<b>Total</b>	<b>2.29</b>	---	<b>1.66</b>	---	<b>1.38</b>	---	---	---
<i>Furan</i>								
2-Furancarboxaldehyde, 5-methyl-	1.12	1.15	1.23	1.15	1.03	---	1.18	---
2-Furanmethanol	6.42	7.11	5.18	6.36	5.12	6.72	5.82	6.72
3-Acetyl-2,5-dimethyl furan	---	1.12	---	---	---	---	---	---
4(5H)-Benzofuranone, 6,7-dihydro-3,6-dimethyl-, (R)-	---	1.28	---	---	---	---	---	---
Benzofuran, 2,3-dihydro-	15.79	21.16	13.64	17.98	10.2	21.73	13.81	21.09
Furfural	2.33	2.34	2.95	2.27	3.06	2.78	2.95	2.32
<b>Total</b>	<b>25.66</b>	<b>34.16</b>	<b>23.0</b>	<b>27.76</b>	<b>19.41</b>	<b>31.23</b>	<b>23.76</b>	<b>30.13</b>
<i>Ketones</i>								
1-(4-methylthiophenyl)-2-propanone	---	---	1.14	1.18	---	---	---	---
1,2-Cyclopentanedione	2.35	2.76	---	2.65	---	2.58	---	2.38
1,2-Cyclopentanedione, 3-methyl-	4.04	4.29	3.3	3.7	3.73	3.08	3.8	2.86
1-Hydroxy-2-butanone	---	1.76	---	1.63	---	1.86	---	1.62
2-Cyclopenten-1-one	1.18	---	1.16	---	1.25	---	1.44	---
2-Cyclopenten-1-one, 2,3-dimethyl-	1.1	---	0.96	---	1.01	---	0.88	---
2-Cyclopenten-1-one, 2-hydroxy-	---	---	2.26	---	1.89	---	1.64	---
2-Cyclopenten-1-one, 2-methyl-	---	---	0.83	---	0.92	---	1.01	---
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.59	2.04	1.51	1.86	1.52	1.51	1.5	1.44
2-Cyclopenten-1-one, 3-methyl-	1.21	---	1.02	---	1.17	---	1.35	---
Ethanone, 1-(2-furanyl)-	---	---	0.99	---	1.07	---	0.97	---
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.14	1.29	1.54	1.57	1.21	1.94	0.92	1.68
<b>Total</b>	<b>12.61</b>	<b>12.14</b>	<b>14.71</b>	<b>12.59</b>	<b>13.77</b>	<b>10.97</b>	<b>3.51</b>	<b>9.98</b>
<i>Phenols</i>								
1,2-Benzenediol, 3-methoxy-	1.67	2.01	1.58	2.01	1.46	---	1.44	---
1,2-Benzenediol, 3-methyl-	---	---	---	---	---	---	0.85	---
2-Methoxy-4-vinylphenol	6.69	7.65	5.49	7.85	3.74	9.32	5.1	8.83
5-tert-Butylpyrogallol	---	---	2.11	---	---	1.94	---	---
Catechol	2.52	2.17	1.99	3.86	2.23	4.22	2.8	2.84
Creosol	1.88	1.61	2.25	2.03	2.11	1.94	1.76	1.92
Hydroquinone	---	---	---	1.85	---	---	---	---
Phenol	5.82	5.73	5.04	5.27	7.19	4.23	7.86	4.98
Phenol, 2,4-dimethyl-	5.95	---	---	---	0.75	---	0.96	---
Phenol, 2,6-dimethoxy-	---	6.13	7.75	6.92	6.66	7.9	4.94	7.76
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	2.21	2.04	3.19	3	1.98	3.52	1.78	3.3
Phenol, 2-methoxy-	9.09	8.5	9.48	8.97	10.13	8.27	10.1	8.63
Phenol, 2-methoxy-4-(1-propenyl)-	---	---	2.24	---	---	---	---	---
Phenol, 2-methyl-	2.9	2.08	2.01	2.26	3.16	2.5	3.3	2.88
Phenol, 3-ethyl-	---	2.8	---	4.62	1.12	3.4	---	3.43
Phenol, 4-ethyl-	7.45	---	4.69	---	5.79	---	5.79	---
Phenol, 4-ethyl-2-methoxy-	5.13	5.12	4.17	2.54	4.48	2.16	4.63	4.46
trans-Isoeugenol	1.79	1.93	---	2.08	1.65	2.26	1.64	2.16
Vanillin	---	---	0.95	---	0.85	---	0.9	---
<b>Total</b>	<b>53.10</b>	<b>47.77</b>	<b>52.94</b>	<b>53.26</b>	<b>53.3</b>	<b>51.66</b>	<b>53.85</b>	<b>51.19</b>

### 3.5. FT-IR analysis of feedstock and solid/liquid products

The FT-IR spectra of the feed, sorghum straw and the bio-oils along with their biochars obtained from the slow pyrolysis at an optimized pyrolysis condition of 350°C and 400°C in the environments of nitrogen and carbon dioxide respectively is shown in figure 6. The spectra showed no significant variations in the curve of bio oils and the bio chars of different atmosphere. The appearances of band at 2970 cm<sup>-1</sup> and at 1430 cm<sup>-1</sup> corresponds to the C-H stretching and bending respectively, indicating the presence of aliphatic hydrocarbons. An intense signal is obtained for it in the bio-oils while, almost negligible in the case of bio-

chars. Small bands in range of 1100-1400 cm<sup>-1</sup> observed in the case of bio-oils are for the stretching of C-O or C-C-O group in alcoholic or alkoxide substituents that are probably, due to phenols and phenolic ethers like cresol, catechol. The other sharp peaks around 1500-1600 cm<sup>-1</sup> in bio-oils are for the C=C stretching that are a part of aromatic rings. Existence of these aromatic structures in the bio-oils indicates the possibility of the condensation reactions that might have occurred during the pyrolysis, signifying the reformation of the macromolecular structure present in biomass. The appearance of the intense broad bands in the region of 3300-3500 cm<sup>-1</sup> attributes to the stretching due to O-H groups

**Table 3.** Physicochemical properties of biochar

Proximate analysis	N <sub>2</sub>	CO <sub>2</sub>
Moisture, wt%	—	—
Volatiles, wt%	25.64	27.67
Fixed carbon, wt%	62.96	59.88
Ash, wt%	11.40	12.45
Elemental analysis (wt.%, dry-ash-free basis)		
C, wt%	68.63	65.90
H, wt%	3.93	3.668
N, wt%	0.83	0.43
S, wt%	0.25	0.05
O, wt% (By difference)	26.36	29.95
Heating value		
HHV, MJ/kg	27.96	26.65

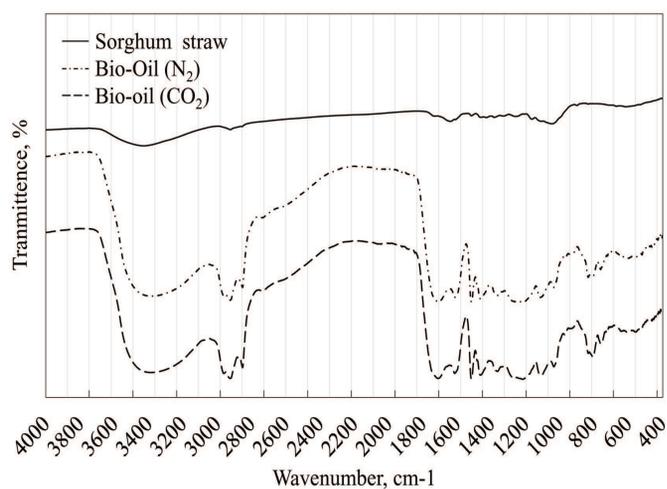
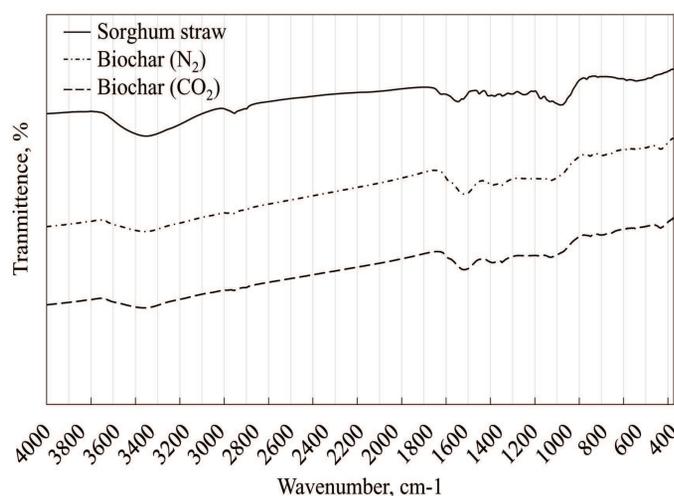


Figure 6(a)

**Figure 6.** Comparison of FT-IR spectrum of sorghum straw feedstock with: (a) bio-oil obtained in N<sub>2</sub> and CO<sub>2</sub> atmospheres, (b) biochar obtained in N<sub>2</sub> and CO<sub>2</sub> atmospheres

present in the feed. In the case of biochars, intensity of this peak is diminished as compared to the feed thereby, identifying that the hydroxyl groups are involved in hydrogen bonding. The presence of these peaks in addition to the peaks due to C=O stretching vibrations between 1700-1750 cm<sup>-1</sup> confirms the presence of carbonyl compounds such as ketone, aldehyde, carboxylic group and their derivatives; which were not evident both in GC-MS and <sup>1</sup>H-NMR (Krishna et al., 2016). Presence of other peaks in bio-oils show wide range of functionalities that are present in the bio-oils produced.

#### 4. Conclusions

Sorghum straw is a potential feedstock among the agricultural wastes for the production of renewable fuels/chemicals. Pyrolysis of sorghum straw was performed in the temperature range of 300 to 450°C, in N<sub>2</sub> and CO<sub>2</sub> environments, and ambient pressure. The experiments were conducted to investigate the effect of temperature and reaction environment on the product behavior. Maximum yield of bio-oil was obtained at 350°C for N<sub>2</sub> environment, and at 400°C for CO<sub>2</sub> environment. Bio-oils obtained in both the environments were mainly constituted of ketones, furans, phenols, and their derivatives. More furans but less ketones were formed in the CO<sub>2</sub> environment. The compounds obtained in the bio-oil are of industrial importance and can substitute the chemicals produced via conventional processes, thus providing a green route for their synthesis.

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